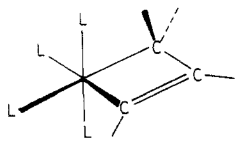
$CSC(CF_3)C(CF_3)S$ heterocycle. To achieve a simple but useful description of the complicated structure of 1, the concept of isolobal analogy[9] is used. The fragment (triphos)ClRh(I) may be taken as a $d^8$ $L_4M$ fragment with $C_{2v}$ symmetry, which in turn is isolobal with $CH_2$. Thus the skeleton 3 of the complex may be related to a cyclobutene derivative, 4. This description is supported by the value



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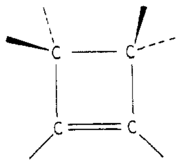
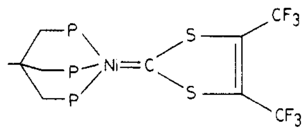


4

of the C(7)–C(8) double bond distance of 1.30 (4) Å and by the almost tetrahedral geometry about C(6). The latter atom is displaced ca. 0.39 Å from the plane of the $CS_2C_2$ ring, and such a deformation from planarity is another evidence of the strong tendency of C(6) toward $sp^3$ hybridization. Accordingly, we may consider this compound as a new unusual example of a spirane-like organometallic structure where C(6) is shared by two cyclic groups.

In the absence of kinetic measurements as well as of detectable intermediates, it should be hazardous to propose a detailed mechanism for the formation of 1. Tentatively, a reasonable reaction pathway is the one shown in Scheme I, in which the intermediacy of a dithiocarbene complex of type 3 is hypothesized. As mentioned above, in fact, the formation of 1,3-dithiol-2-ylidene complexes by reaction of $\eta^2$-$CS_2$ compounds with activated alkynes is quite common. In particular, the compounds (triphos)Ni[$CS_2C_2(CF_3)_2$][3d] (5) and ($np_3$)Ni[$CS_2C_2(CF_3)_2$][3e] (6) have been obtained by reacting $F_3CC\equiv CCF_3$ with (triphos)Ni($\eta^2$-$CS_2$) and ($np_3$)Ni($\eta^2$-$CS_2$), respectively. Unfortunately, all our attempts to isolate the 1,3-dithiol-2-ylidene derivative were unsuccessful.



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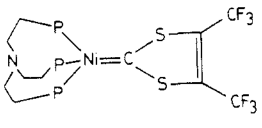

This communication reports a new reaction of $\eta^2$-$CS_2$ metal complexes and might provide useful information on alkene and alkyne metathesis reactions. Key intermediates of these reactions are believed to be, in fact, metallacyclobutane or metallacyclobutadiene complexes which may be formed by metal-assisted coupling of alkenes or alkynes with carbene or carbyne ligands.[10]

**Registry No.** 1, 94070-31-2; 2, 92669-51-7; hexafluorobut-2-yne, 692-50-2.

**Supplementary Material Available:** Listings of atomic parameters for (triphos)ClRhC($CF_3$)=C($CF_3$)CSC($CF_3$)=C($CF_3$)S (Tables I and II) and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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# Vinyloxomolybdenum(VI) Complexes Produced by Protonation of Coordinated Acetylenes[†]

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*Summary:* Vinyloxomolybdenum(VI) complexes have been prepared from substituted acetylene adducts of $OMo(S_2CNMe_2)_2$ by stereospecific protonation with trifluoroacetic acid and characterized by elemental analysis and IR and NMR spectroscopy. The isolation of these compounds suggests routes for the catalyzed reduction of acetylene by both nitrogenase and certain model systems for this enzyme.

Because $C_2H_2$ is a substrate of nitrogenase,[1] studies of the binding and subsequent reduction of acetylenes in model systems may be relevant to the understanding of the mechanism of action of this enzyme. Of particular interest is the chemistry of molybdenum–acetylene complexes because it is commonly believed[2-5] that this metal binds the nitrogenase substrates. It is certainly a constituent of FeMo-co,[6-8] the substrate-reducing prosthetic group of nitrogenase.[9] Previously,[3,10-12] we reported the preparation of $OMo(S_2CNMe_2)_2(CH_3O_2CC\equiv CCO_2CH_3)$ (1) from $OMo(S_2CNMe_2)_2$ and dimethyl acetylenedicarboxylate and the analogous adducts of ditoluoylacetylene ($CH_3C_6H_4COC\equiv CCOC_6H_4CH_3$) (2), methyl propiolate ($HC\equiv CCO_2CH_3$) (3), and of $C_2H_2$ itself. Their varying reactivities and the X-ray structural characterization of 2 have been reported also.[10-12] Herein, we report the protonation of 1, 2, and 3 with trifluoroacetic acid to form vinyloxomolybdenum(VI) complexes. Closely related reactions have been reported[13] for $Mo(C_2R_2)_2(S_2CNR'_2)_2$. These new compounds extend a very short list of vinylmolybdenum compounds with extreme examples[14,15] being

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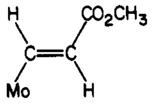
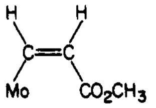
($\eta^5$-$C_5H_5$)Mo[P(OMe)$_3$]$_3$[HC=CH($t$-Bu)] and $MoO_2Br$(bpy)(HC=$CH_2$). Such compounds may provide insight into the mechanism of reduction of acetylene to ethylene by both nitrogenase[1] and certain proposed[15,16] model systems for this enzyme.

Addition of an excess of $CF_3CO_2H$ (0.30 mL) to a solution of **3** (0.30 g) in $CHCl_3$ (30 mL) results in the immediate formation of a yellow solution from which a yellow microcrystalline solid (**4**; 83% yield) is isolated after evaporation to dryness and trituration of the residue with diethyl ether. Elemental analysis[17] indicates that **4** should be formulated as $OMo(S_2CNMe_2)_2(HC{=}C(H)CO_2CH_3)(CF_3CO_2)$. Conductivity measurements ($\Lambda$ = 7.3 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for a $10^{-4}$ M acetone solution) show the complex to be a nonconductor,[18] thus implying coordination of trifluoroacetate to molybdenum and preservation of its heptacoordination. The IR spectrum of **4** contains bands at 960 ($\nu$(Mo=O)), 1710 (broad with shoulders, $\nu$(C=O) of both HMP and $CF_3CO_2$), and 1550 cm$^{-1}$ ($\nu$(C=N)). The vinyl $\nu$(C=C) could not be assigned because it is either very weak or obscured by the $\nu$(C=O) or $\nu$(C=N) absorptions. Previously,[19] the C=C stretch in vinylplatinum complexes was assigned at 1590 cm$^{-1}$.

The NMR spectrum ($CDCl_3$) of **4** contains a resonance at $\delta$ 3.85 (intensity 3) assigned to the methyl protons of the vinyl group and four resonances ($\delta$ 3.62, 3.55, 3.50, 3.47; intensity 3:3:3:3) assigned to the magnetically inequivalent $N$-methyls of the dithiocarbamate ligands. The olefinic protons of the vinyl group appear as an AB pattern at $\delta$ 6.28 (intensity 1) and 4.59 (intensity 1) and $J_{AB}$ = 12.3 Hz. Two isomeric structures of the vinyl group, A and B, are

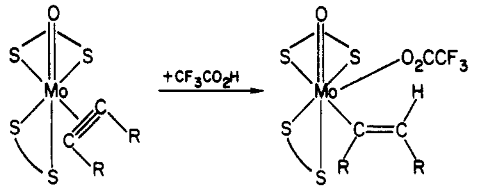


A



B

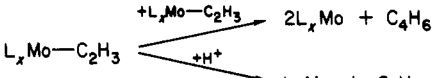
possible, which are often differentiated by the coupling constant of the vicinal protons. Isomers with cis protons usually have $J_{AB}$ = 5–14 Hz, while the range 11–19 Hz is found for $J_{AB}$ in isomers with trans protons.[20] Unfortunately, the observed value of 12.3 Hz is intermediate between the two ranges and obviously cannot be used to define the olefinic stereochemistry. However, nucleophilic additions to metal-bound alkynes usually occur[21] trans to the metal to give a stereochemistry equivalent to B, while electrophilic addition (protonation) to platinum–alkyne complexes[19,22] produces a vinyl species with the proton cis to the metal as in A above. These data suggest stereochemistry A for **4** (eq 1), but as we have, as yet, been unable to grow crystals suitable for X-ray structural investigations, this problem remains unresolved. The protonation of **3** is, however, completely stereospecific because the NMR spectrum of a homogeneous reaction mixture of **3** and $CF_3CO_2H$ shows only a *single* AB pattern for the vinyl protons.



(1)

The similar protonation of **1** and **2** with $CF_3CO_2H$ gives the analogous yellow vinyloxomolybdenum(VI) complexes $OMo(S_2CNMe_2)_2(CH_3O_2CC{=}C(H)CO_2CH_3)(CF_3CO_2)$ (**5**; 84% yield) and $OMo(S_2CNMe_2)_2(CH_3C_6H_4C(O)C{=}C(H)C(O)C_6H_4CH_3)(CF_3CO_2)$ (**6**; 60% yield), again with complete stereospecificity.[17] Their NMR spectra contain single resonances for the vinyl protons ($\delta$ 4.88 for **5** and 6.62 for **6**) and four resonances centered at ca. $\delta$ 3.5 due to the dithiocarbamate methyl groups. As expected, the methyl groups of the vinyl moieties are magnetically inequivalent and appear at $\delta$ 3.83 and 3.75 in **5** and at $\delta$ 2.45 and 2.37 in **6**. Their IR spectra contain bands at ~970 cm$^{-1}$ ($\nu$(Mo=O) and at ~1710 cm$^{-1}$ (broad with shoulders and assigned to $\nu$(C=O) of both the vinyl group and $CF_3CO_2$).

Similar vinylmolybdenum complexes could explain the variation in observed products of acetylene reduction by the "molybdothiol catalyst" system.[15,16] Corbin et al.[16] found both butadiene and ethylene, while previous reports[15] had indicated only ethylene and traces of ethane as products. The intermediacy of a vinylmolybdenum complex (C) would account for both reduction products because the vinyl group could dimerize (eq 2), particularly in concentrated solutions,[15,16] to yield $C_4H_6$ or could be further protonated (eq 3) to produce $C_2H_4$. The dimerization reaction (eq 2) finds support in the thermal decomposition of silver(I)- and copper(I)-vinyl complexes, both of which yield the corresponding free diene.[23]



C

(2)

(3)

Finally, it should be noted that several mechanisms have been suggested[2,4,5,15,24,25] for substrate reduction ($C_2H_2$ to $C_2H_4$ or $N_2$ to $2NH_3$) by nitrogenase, which involve protonation subsequent to addition to molybdenum in a sequence of one- or two-electron and proton steps. These suggestions gain support from our results, which also suggest that the absence of product butadiene in nitrogenase-catalyzed acetylene reduction[16] is consistent with the enzymic molybdenum-containing, substrate-reducing sites being monomeric and well separated. Further, the stereospecificity exhibited in the protonation of **1**, **2**, and **3** is consistent with the exclusive production of cis olefins by nitrogenase.[1]

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**Registry No.** **1**, 39584-77-5; **2**, 73367-37-0; **3**, 73367-33-6; **4**, 94325-06-1; **5**, 94325-08-3; **6**, 94325-10-7.

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(17) $OMo(S_2CNMe_2)_2(HC{=}C(H)CO_2CH_3)(CF_3CO_2)$. Anal. Calcd for $C_{12}H_{17}F_3MoN_2O_5S_4$: C, 26.2; H, 3.09; N, 5.09. Found: C, 25.7; H, 3.03; N, 5.10. $OMo(S_2CNMe_2)_2(CH_3O_2CC{=}C(H)CO_2CH_3)(CF_3CO_2)$. Anal. Calcd for $C_{14}H_{19}F_3MoN_2O_7S_4$: C, 27.6; H, 4.61; N, 3.13. Found: C, 27.7; H, 4.56; N, 3.02. $OMo(S_2CNMe_2)_2(CH_3C_6H_4C(O)C{=}C(H)C(O)C_6H_4CH_3)(CF_3CO_2)$. Anal. Calcd for $C_{26}H_{27}F_3MoN_2O_5S_4$: C, 42.9; H, 3.85; N, 3.71. Found: C, 42.3; H, 3.85; N, 3.58.

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